A Quality Control Procedure Specialized for Incremental Sampling

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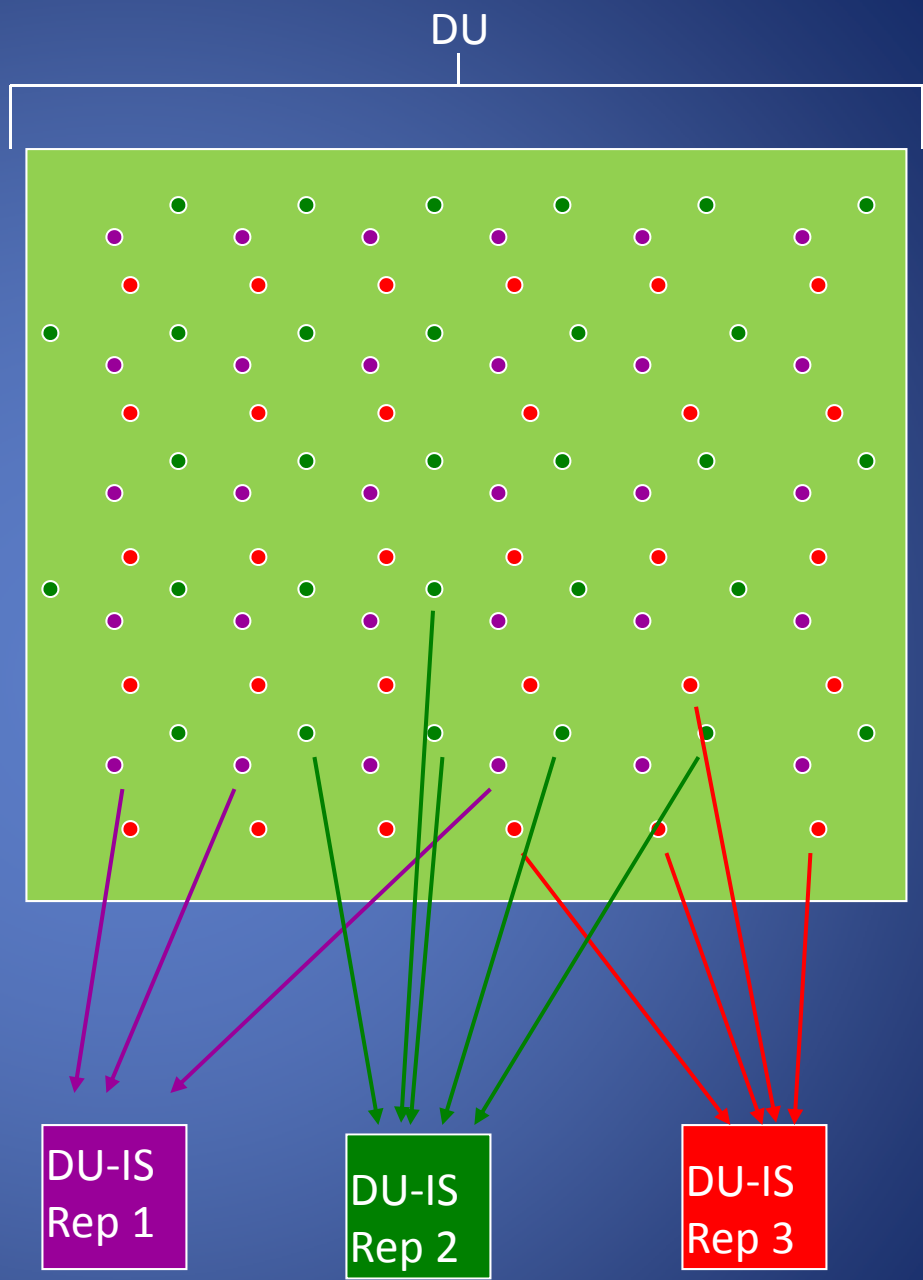
Quality Assurance for Incremental Sampling Designs

- QA should be an IMPORTANT facet of IS designs
- 3 replicates (triplicates) are commonly used to calculate a UCL; they also provides a metric enabling assessment of overall quality
- If all other sources of data variability have been controlled, but triplicates do not agree well enough to make a decision, the problem is probably too few increments to sufficiently control the within-DU heterogeneity

Triplicate incremental samples taken over a single DU



3 replicate DU-ISs of 30 increments each

Evaluating Sources of Data Variability

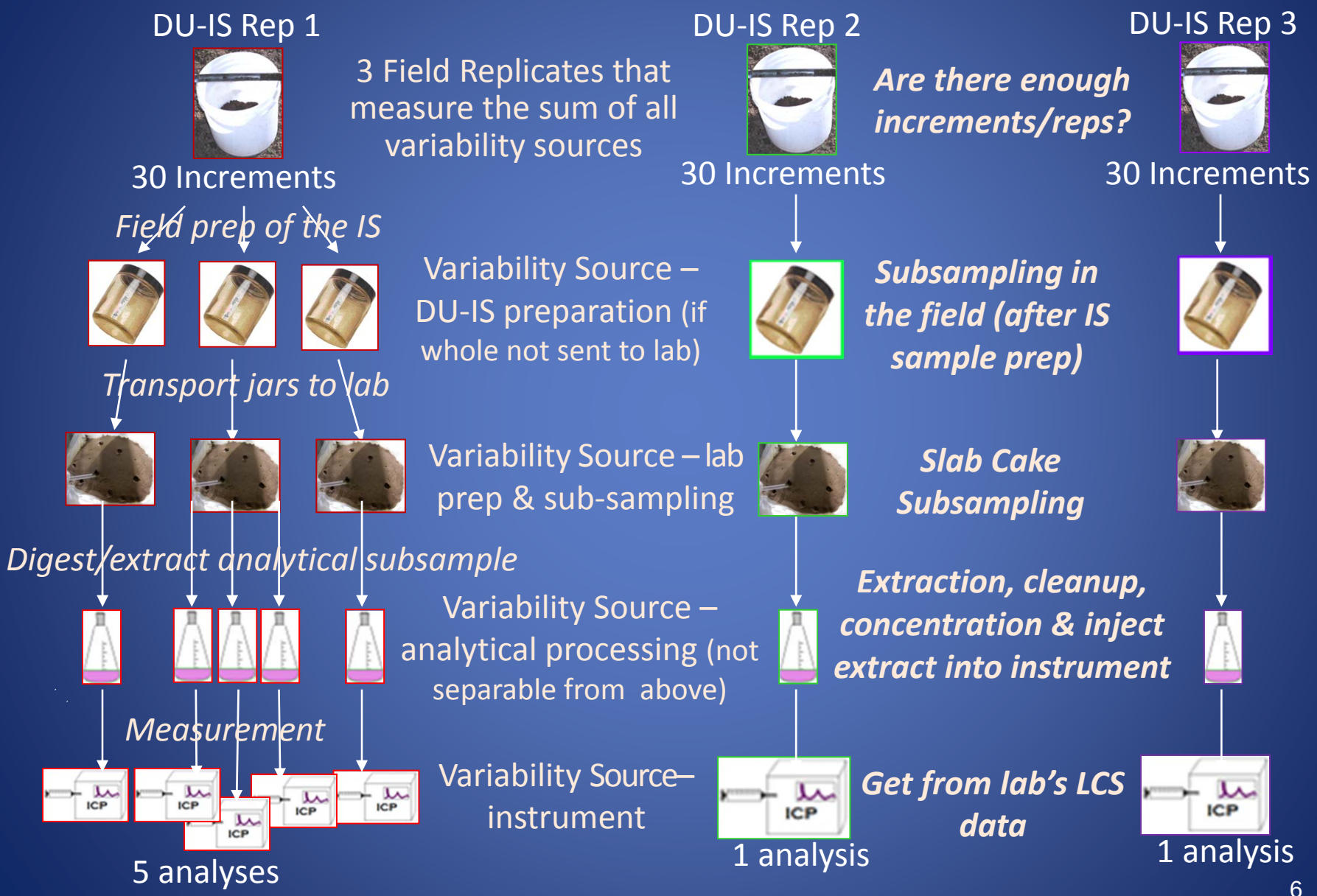
- Measuring the strengths of different sources as a QC mechanism for sampling design & sample handling
  - Based on a series of triplicates that isolate and measure the performance of each major step in the sample handling sequence
- If data uncertainty is too great to support decision-making, shows where to target corrective action
  - All for the cost of 4 additional analyses

Definitive Data Include Error Measurement

The definition of "definitive data" in the *"DQOs for Superfund"* 1993 guidance (p. 43) includes this statement:

"For the data to be definitive, either analytical or total measurement error must be determined."

Replication QC Procedure



Calculations

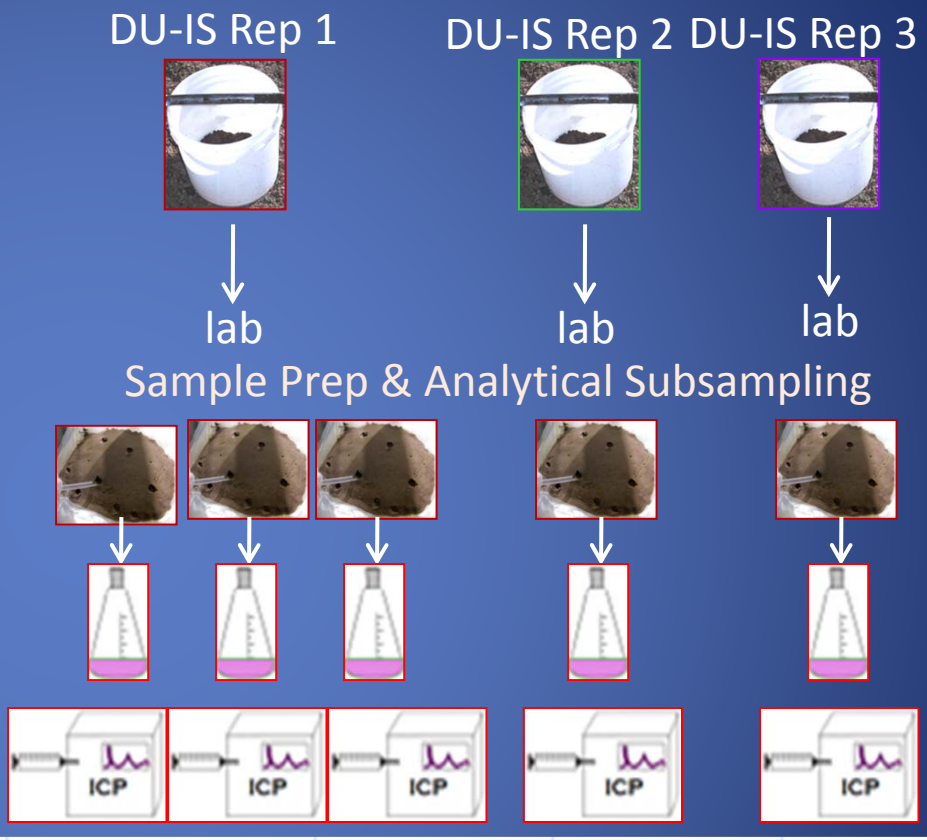
- Theoretical equation:

$$SD_{Total}^2 = SD_{LCS\text{-}instrument}^2 + SD_{analytical\ subsample}^2 + SD_{IS\ prep}^2 + SD_{bet\text{-}IS\ samples}^2$$

- In actual projects, likely will not get all the information needed to partition variability to 4 sources
- Actual data example to illustrate

Example from Actual Data

- 3 replicate IS samples collected
- 3 replicate analytical subsamples
- For Sb, As & Pb, field heterogeneity was dominant error



ANALYTE	Total measurement error (SD)	Total measurement error (%RSD) (SD/mean*100)	Analytical + sample proces-sing error (SD)	Analytical + sample proces-sing error (%RSD)	Field-scale (between-IS) error (SD)	Field-scale (between-IS) error (%RSD)
ANTIMONY	0.43	37	0.038	5	0.43	27
ARSENIC	0.76	19	0.39	11	0.66	14
LEAD	67	22	17	7	65	17

Calculation

- Total Error (as Std Dev) obtained from field IS replicates
- Sample Prep/Subsampling Error (as Std Dev) obtained from subsampling replicates
- Field-scale between-IS Error (as Std Dev):

Field-scale Error = sqrt(Total Error^2 - Subsampling Error^2)

ANALYTE	Total measurement error (SD)	Total measurement error (%RSD) (SD/mean*100)	Analytical + sample proces-sing error (SD)	Analytical + sample proces-sing error (%RSD)	Field-scale (between-IS) error (SD)	Field-scale (between-IS) error (%RSD)
ANTIMONY	0.43	37	0.038	5	0.43	27
ARSENIC	0.76	19	0.39	11	0.66	14
LEAD	67	22	17	7	65	17

Is Variability Within Acceptable Limits?

- Depends
  - If determining UCL to use as EPC for RA, is there a significant difference in risk if mean vs UCL used? Is it worth it to reduce variability to bring UCL closer to mean? (e.g., go back & collect add'l IS reps)
  - If comparing to an action level, do mean & UCL straddle AL? Does critical decision hinge on the UCL?

	MIS Field Replicate 1 - ground	MIS Field Replicate 2 - ground	MIS Field Replicate 3 - ground			
Sample Number :	MIS-DU6-01-06	MIS-DU6-02	MIS-DU6-03			
Sampling Location	MIS-DU6-01	MIS-DU6-02	MIS-DU6-03			
ANALYTE	Result	Result	Result	DU6 average	DU6 total SD	95% UCL(t)
ANTIMONY	0.75	1.6	1.1	1.2	0.4	1.9
ARSENIC	3.1	4.6	4.1	3.9	0.8	5.2
LEAD	244	377	298	306	67	419

Component Can Exceed Total

- Happens when IS field replicates agree better than subsample replicates
- Could be chance or indication that subsampling needs CA

	MIS Field Replicate 1	MIS Field Replicate 2	MIS Field Replicate 3		
	ground	ground	Triplicate Lab Post-grind Subsamples		
Sample Number :	MIS-DU3-01	MIS-DU3-02	MIS-DU3-03-01	MIS-DU3-03-02	MIS-DU3-03-03
Sampling Location :	MIS-DU3-01	MIS-DU3-02	MIS-DU3-03	MIS-DU3-03	MIS-DU3-03
ANTIMONY	0.89	1.3	1.3	1.9	1.4
ARSENIC	4.2	4.6	4.6	5.1	4.8
LEAD	177	177	213	290	273

Analyte	Total measurement error (SD) use 1st subsmpl rep	Total measurement error (%RSD) (SD/mean*100)	Analytical + sample proces-sing error (SD)	Analytical + sample proces-sing error (%RSD)	Field-scale (between-IS) error (SD)	Field-scale (between-IS) error (%RSD)
ANTIMONY	0.24	19	0.32	21	analytical > total	analytical > total
ARSENIC	0.23	5	0.25	5	analytical > total	analytical > total
LEAD	21	10	40	16	analytical > total	analytical > total

Do As Part of Pilot Study

- A pilot study can provide many benefits
  - Assess sources of data variability
  - If necessary, select corrective actions to reduce largest source
  - Use opportunity to fill CSM gaps or test critical assumptions underlying the sampling design
  - Determine optimal number of increments and/or number of IS field replicates
  - Use as readiness review for field & lab staff

Potential Corrective Actions

- Increase mass of increments
- Increase mass of analytical subsamples
- Improve rigor of analytical subsampling
  - Use more Gy “correct” sampling tool
  - Increase number of increments in subsample
- Improve sample handling/homogenization prior to subsampling
  - Break up clods better
  - More “correct” sample volume reduction (e.g., “correct” tool with 1-D slabcake; sectorial splitter)
  - More careful, stringent sieving so particles more uniform
  - Milling
- Increase # of increments and/or IS replicates

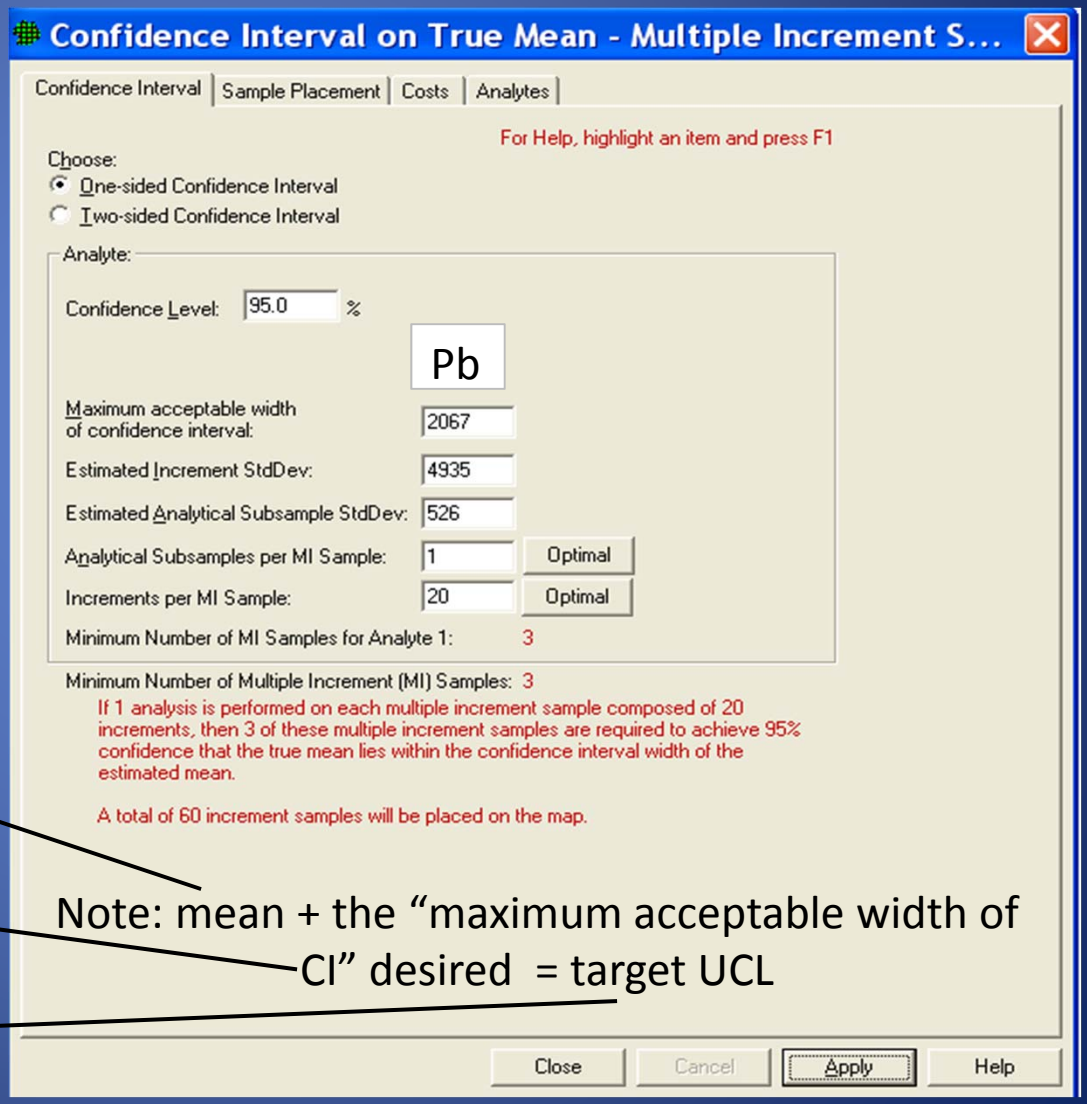
Statistically, How Many Increments?

- Field variability study as part of pilot study
- Need enough discrete samples to run good statistics: ~10
- Must use same discrete sample support as the increment support expected during main study
- Determine field-scale & subsampling error for that matrix and that increment support

Using VSP MIS Module for # Increments

10 discrete samples

Sample #	LEAD
FE-DS-DU4-05	840
FE-DS-DU4-10	8260
FE-DS-DU4-15	28.6
FE-DS-DU4-20	31.5
FE-DS-DU4-25	1040
FE-DS-DU4-30	3020
FE-DS-DU4-35	648
FE-DS-DU4-40	15500
FE-DS-DU4-45	5260
FE-DS-DU4-50	6720
mean =	**4135**
Total std dev =	**4963**
RSD =	**1.20**
1-side CI 1/2-wdth (50%)	**2067**
subsample SD	**526**
increment SD = field SD	**4935**
target 95% UCL (+50%)	**6202**



Note: mean + the "maximum acceptable width of CI" desired = target UCL

Any Questions?